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ROLE OF AMINES IN ADHESION OF POLYBUTADIENE TO GLASS
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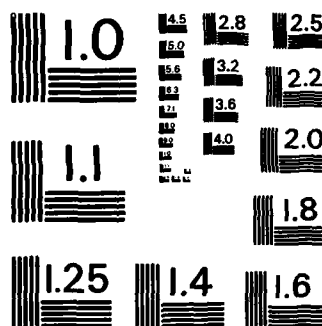
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<p>An attempt to elucidate the role of amines in general, and of 3-amino-propyltriethoxysilane in particular, has been made through a study of the title subject by several different approaches. This paper describes the effect of amine structure and concentration on the strength of adhesion of peroxide cured polybutadiene to a glass surface. It demonstrates that adhesion of polybutadiene to glass surfaces is enhanced by incorporation of small amounts of amines into the elastomer. An 80-fold increase in the work</p>		

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of adhesion was observed in the presence of 3-aminopropyltrimethoxysilane. The results are interpreted in terms of information reported in previous papers in this series.

OFFICE OF NAVAL RESEARCH

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Project NR 092-555

Technical Report No. 25

ROLE OF AMINES IN ADHESION OF POLYBUTADIENE TO GLASS SUBSTRATES

IV. EFFECT OF AMINE STRUCTURE AND CONCENTRATION ON STRENGTH OF ADHESION

by

Y. Eckstein and P. Dreyfuss

Institute of Polymer Science
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Akron, Ohio 44325



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INTRODUCTION

In the course of our earlier studies of the adhesion of polybutadiene to inorganic crystalline substrates and of the physical properties of polybutadiene containing glass bead fillers treated with 3-aminopropyltriethoxysilane, an increase in adhesion was found when amines were present at the interface between the elastomer and the crystals (1) or glass beads (2). Similar observations have been reported in the literature (3-5). Also, in some experimental studies on the adhesion of polybutadiene to various substrates it was observed that amine antioxidants added to the elastomer compound had a profound effect in increasing the level of adhesion (6). The reasons for these increases are not at all apparent. These observations led us to undertake this study of the role of amines in the adhesion of polybutadiene to glass substrates. This paper describes the effect of amine structure and concentration on the strength of adhesion. The results are interpreted on the basis of information gained in earlier studies of model systems (7-9). In paper I of this series, reactions of amines during peroxide curing of polybutadiene were considered and the effects of the addition of very small concentrations of amines on mechanical properties of the cured polybutadiene were studied (7). In paper II of the series reactions of amines with trimethoxysilanol and/or fumed silica were studied by IR, NIR, GLC, ^{13}C NMR, ^1H NMR, MS and one product was characterized by elemental analysis (8). In paper III of the series the effects of amines on the reaction of dicumylperoxide with model olefins were examined (9). The first paper was published earlier and the principal conclusions are

summarized in paper II of the Series. Papers II and III precede this paper and the reader should refer to them for detailed bases of the conclusions from them used in the discussion of adhesion results below.

EXPERIMENTAL

Materials

Most of the materials used in this study have been described in previous papers in this series (7-9). Glass slides were pre-cleaned soda lime microscope slides from B. H. Sargent & Co.

Cleaning of Glass Slides

The glass slides were washed successively with boiling 2% "Microsolution" for 1 hr, distilled water, boiling 1% phosphoric acid for 1/2 hr., distilled water and boiling distilled water for 1/2 hr., before drying at 140°C for 2 hrs and storing in a dessicator over P_2O_5 .

Crosslinking of Polybutadiene (PB)

Amines were incorporated into PB as described in Part I of this series. For adhesion measurements, PB containing amine, was crosslinked with 0.1 phr of peroxide. Before bonding, the elastomer was pressed into a thin layer (~ 0.2 mm) by premolding for 1 hr at 65°C, then pressed into a sheet of cotton cloth and again premolded for 1 hr at 65°C. The cloth backed layer was then pressed against cleaned glass slides for 2 hrs at 149°C in a PHI press at pressure of ~ 6 psi/5" ram. The thickness of the elastomer interlayer in the resulting cloth-elastomer-glass sandwich was 0.2 mm.

Measurement of Work of Adhesion

180° Peeling tests were carried out on strips of cloth backed elastomer layer after trimming them to a uniform width on the glass of 2 cm. The elastomer layer was peeled off the glass at constant rate, 0.5 cm/min (0.0083 cm/sec). The work of adhesion per unit area of interface was calculated from the time average of the peel force P per unit width of the detaching layer: $W = 2P$.

RESULTS

The values of the work of adhesion of PB, blended with different amino compounds, to the glass surface are listed in Table I. The amines used for this part of the study included aniline(A), m-phenylenediamine(PDA), piperazine(P), 1,4-diaminobutane(AB), and 3-aminopropyltriethoxysilane(AS). The data for the work of adhesion of PB containing different concentrations of PDA or AS indicate clearly that the adhesion may be enhanced by increasing the concentration of the amine in the vulcanizate. Thus, for example, at a concentration of 0.5×10^{-4} mole of AS/100g PB, the work of adhesion increased by about 16 J/m² in comparison to peroxide cured PB in absence of the amine. When the concentration of AS was increased by a factor of 4, cohesive failure in the rubber phase was observed. Similar dependence of the work of adhesion on the concentration of PDA was observed; however, much higher concentrations of the amine were needed to produce an effect similar to that of AS. Curiously, when AS is added to the rubber at concentrations calculated to be equivalent to formation of a monolayer of silane on the glass surface (1.85×10^{-6} mole AS/100g PB) the work of adhesion

was not increased. This implies that only part of the AS reacts with the glass surface, while another part is consumed in a reaction with the polymeric phase. Alternatively, since the AS was blended into the rubber rather than applied to the glass surface directly, the inefficiency of the AS as a coupling agent may be caused by slow diffusion.

At equivalent molar concentrations of amine, the order of increase in the work of adhesion of PB to glass was:

$$PB = A < P < AB < PDA \ll AS$$

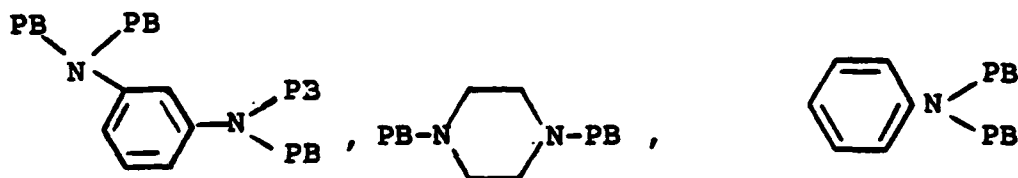
DISCUSSION

Measurements of the mechanical properties of peroxide cured PB in the presence of different amines (7) and studies of model reactions involving (i) amines and silanol groups (8), (ii) amines and peroxides in olefins (9) and (iii) amines, different kinds of double bonds in olefins, peroxides and silanol groups (9) provided information essential for understanding the role of amines in the adhesion of polybutadiene to glass. The studies indicated that the consideration of the mechanism by which amines can react in these systems can be divided for convenience into two parts; namely, reactions involving aromatic amines and piperazine and reactions involving aliphatic amines.

Aromatic Amines and Piperazine

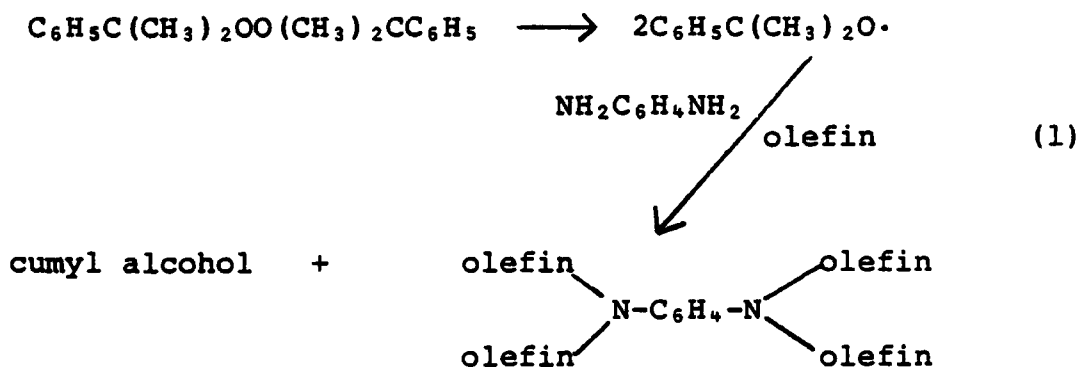
Measurements of mechanical properties (7) showed that tensile strength and crosslink density of peroxide cured PB are enhanced by the presence of aromatic amines and piperazine as long as the

concentration of amine is of the same order of magnitude as that of the peroxide. (At higher molar ratios of amine to peroxide, the amine serves as a radical trap.) The order of enhancement was $PDA > P > A \approx 0$, which is the same as the order of increase in the work of adhesion shown in Table I. The maximum enhancement occurred when the molar concentration of labile hydrogens of the amine was equal to the molar concentration of alkoxy radicals derived from the peroxide. We concluded on the basis of the results reported in previous papers (7-9) that the amines participate in the cross-linking reaction to form networks including structures of the following form:



Thus the diamines led to additional crosslinks and the primary diamine, PDA, linked four chains while the secondary diamine, P, linked two. With the diamines the rings become part of the crosslinks and reduce the flexibility of the chains in the region of the crosslinks. According to Pluddemann's hypothesis (10), increased crosslinking and increased rigidity of the interface are essential for good adhesion in a glass resin system. By the same reasoning the monamine, A, acting in the same way contributed little or nothing to either the tensile strength or the work of adhesion because it became part of the straight chain (7-9).

Studies of the effect of PDA on the reaction of dicumyl peroxide with the olefins 1-decene or 2-hexene supported the mechanism suggested (9). In both systems the amount of cumyl alcohol formed as a result of decomposition of the peroxide according to equation 1:

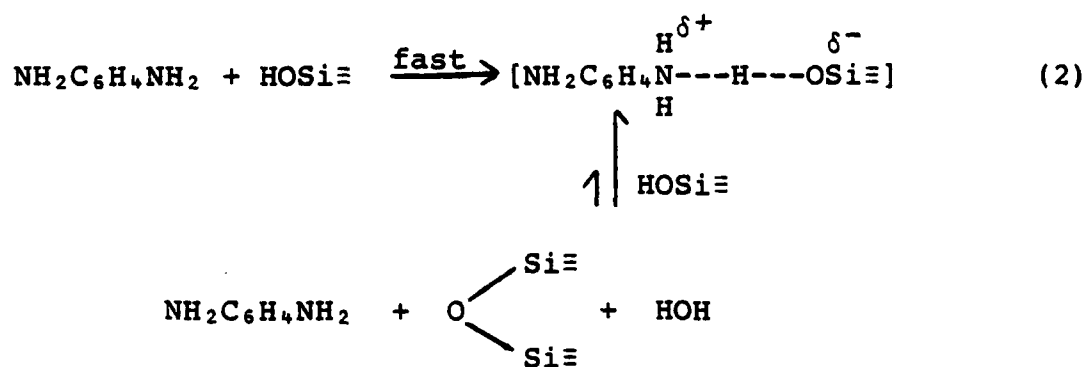


was four or more times higher than that observed in the reaction of the olefin alone with peroxide even though only 50% of the total concentration of amine and olefin were consumed. The concentration of cumyl alcohol was also twice as great as that formed in a comparable reaction between AS and dicumyl peroxide. Presumably all four hydrogens are available for abstraction by the cumyl radical. In our reaction mixtures the amine itself reacted with the olefin to give a second insoluble phase.

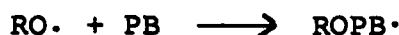
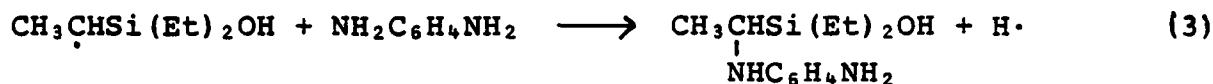
Supporting evidence for the cleavage of the N-H bond rather than the C-N bond of the amine is found in the work of Nazaki and Bartlett (11), who found that when benzoyl peroxide decomposes in amines, the products formed are characteristic of N-H scission. Additional evidence for the formation of C-N bonds comes from the work of Lewis and Correa (12), who reported that the photochemical

reaction of singlet 9-phenanthrenecarbonitrile with diethylamine in nonpolar solvents yields a diethylaminyl radical exclusively and the principal product formed is the addition product 9-(9-diethylamino-9,10-dihydro)phenanthrene carbonitrile. Thus the total evidence is strong that the amine becomes chemically bonded to the PB, a comparatively nonpolar medium.

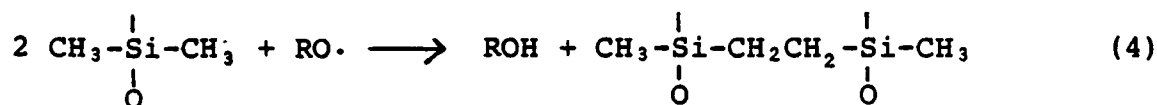
Bonding of the amine to the PB is not sufficient alone to account for the improved adhesion shown in Table I. The interactions between the amine and the -SiOH groups on the glass needs to be considered also. Model reactions between -SiOH groups on either Et_3SiOH or Cab-O-Sil (8) in the absence of peroxide showed that the PDA serves only as a catalyst for the condensation of the -SiOH groups and the concentration of PDA remains unchanged as shown in equation 2:



In the presence of peroxide, the concentration of amino groups decreased dramatically and the concentration of cumyl alcohol was lower by a factor of two (9). The second amine group appeared to react with the silanol to form a chemical bond as shown schematically in equation 3 for one ethyl group and one nitrogen on the amine:

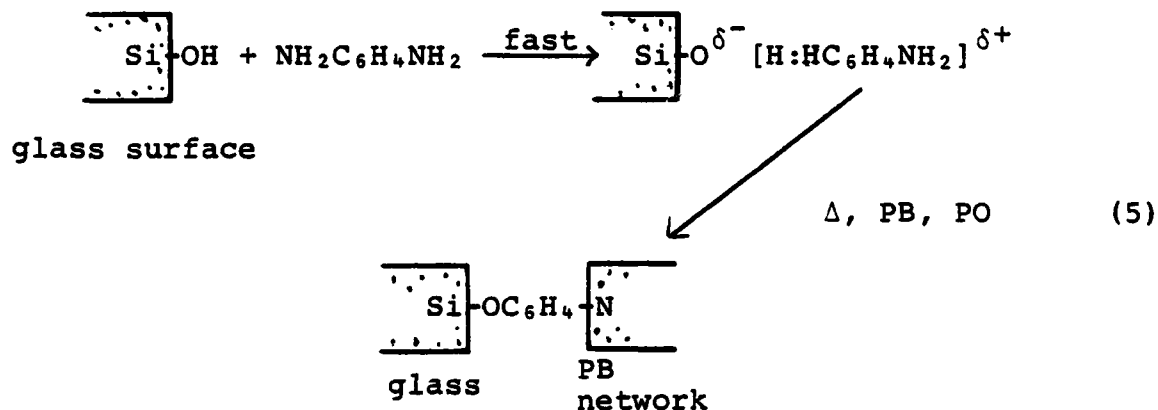


These reactions are analogous to the peroxide curing of polyorgano-silanes shown in equation 4 (13):



but instead of combination of alkyl radicals, trapping of the radical by the amine occurs.

Glass (Cab-O-Sil) does not have any alkyl groups. Model studies (8) have shown that the first reaction in the series of equations 5 occurs.



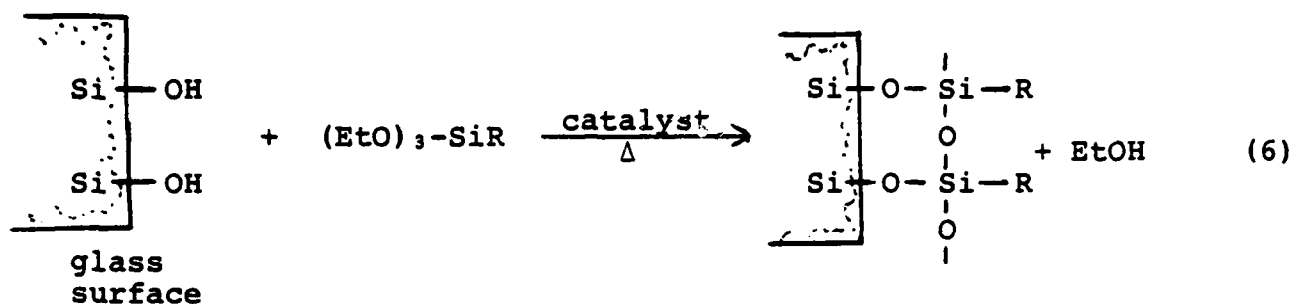
The ionic bonding alone can account for reducing the number of NH_2 groups available for reaction with the PB and peroxide. It can probably also account for the observed increase in the work of adhesion in the presence of PDA. Formation of a true covalent bond of the type shown in the second reaction might occur under curing conditions; however, we have no evidence that such scission takes place in our systems.

Aminosilanes and Acyclic Aliphatic Amines

The work of adhesion of PB to glass was increased almost twofold by the addition of AB, a diamine. The effect was about the same as that of PDA and the mechanism by which adhesion is improved is probably similar to that of PDA. In addition, model compound studies (8) showed that acyclic aliphatic amines in general have a marked tendency to form carbamates (carbon dioxide adducts of amines) and that carbamates enhance the reactivity of the aliphatic amines. This may account for the high reactivity of AB. Again model compound work reported in previous studies by others supports these conclusions (11, 14). The work of Nazaki and Bartlett (11) indicates reaction at the N-H bond rather than at the C-N bond.

Addition of AS to the PB had an outstanding effect on the work of adhesion of PB to glass. (See Table I). Added at much lower levels than any of the other amines in this study, AS nevertheless had by far the greatest effect at improving adhesion. At sufficiently high concentration, its addition resulted in cohesive failure in the PB. Since AS has only one amino group and that group is not very different from those already described, the difference must arise from the three ethoxy groups and their interaction with the glass surface and the PB.

Numerous studies indicate that, mechanistic considerations aside, ethoxysilanes can react with -SiOH groups to form chemical bonds and that further condensation of the ethoxy group leads to a polysiloxane coating on the glass (10, 15-18). The overall reactions are shown schematically in equation 6.



Thus with AS covalent bonds with a glass surface are known to form through oxygen. The new work reported in reference 8 shows that bonds can also form through the amine group as well by the mechanism outlined above. Consequently, the AS bonds to the glass surface with multiple attachments and applied stresses act on a polysiloxane network rather than on isolated bonds.

The remaining question is whether AS can bond to the PB. We have seen that it can do so through the amine group. In addition model compound reactions between AS and peroxide indicate that the ethoxy groups are also susceptible to attack by free radicals (9). Relatively large quantities of cumyl alcohol, more than can be accounted for by reaction of the two hydrogens on the n-propyl group, form (9). When 1-decene was also present, most of the 1-decene polymerized, little ethanol formed, and the primary amine was totally consumed (9). Reaction of AS with 1-decene by a free radical mechanism cannot be excluded. We conclude that the AS is so effective at improving adhesion of peroxide cured PB to glass because there are mechanisms by which all four functional groups on the silicon atom of AS can react with both the substrate and the polymeric resin.

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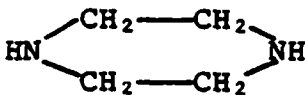
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13 .
TABLE I

Work of Adhesion of Peroxide Cured PB to a Glass Surface in
The Presence of Amines

Amine ^a	Structure	Amine concentration x10 ⁴ mole/100g PB	W _a (J/m ²)	$\frac{W_A^{\text{Amine}^b}}{W_A^{\text{PB}}}$
-	-	-	6.2	1.0
A	C ₆ H ₅ NH ₂	4.0	6.2	1.0
PDA	1,3-C ₆ H ₄ (NH ₂) ₂	2.0	8.6	1.4
PDA	"	3.8	13.0	2.1
P		4.0	7.9	1.3
AB	(NH ₂ CH ₂ CH ₂) ₂	4.0	11.0	1.8
AS	(EtO) ₃ Si(CH ₂)NH ₂	0.0185	6.2	0
AS	"	0.46	22.3	3.6
AS	"	2.0	490.0 ^c	79.0
S	Et ₃ SiOH	3.9	6.1	1.0

^aA = aniline, PDA = m-phenylenediamine, P = piperazine,
AB = 1,4-diaminobutane, AS = 3-aminopropyltriethoxysilane,
S = triethylsilanol

^b $\frac{W_A^{\text{amine}}}{W_A^{\text{PB}}}$ = work of adhesion with added amine/work of adhesion
without added amine

^cCohesive failure in the PB phase was observed

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